OR-17

STRUCTURAL AND THERMODINAMIC MODEL OF CATIONIC DYE ADSORPTION ON THE NANOCLUSTER POLYOXOMETALATE SURFACE

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Abstract. The giant nanocluster polyoxomolybdates (POM), with Keplerate – Mo_{132}***(1)*** and toroidal – Mo_{138}***(2)***structures, were used as the inorganic macroanionic templates for rhodamine-B (RhB) monolayer formation from the aqueous solution (C_1=4.2×10^{-6}M, C_2=2.7×10^{-6}M). The UV-Vis spectra shown the increasing of dye H-aggregate's fraction on the POM surface when RhB concentration risen. Furthermore, the appearance of a new signal (~590nm) corresponds to presence of the J-aggregates that is in line with fluorescence spectroscopy data. Namely, during J-aggregates formation on the POM surface, the emission signal gradually grows, as compared to quenched signal from RhB's monomer forms, and shifts on 30–40 nm to 612–620 nm. In addition, in photoluminescence excitation spectra a new short-wavelength band reveals near 505–512 nm that relates to electron transition from S_0 to new S_2 state arising out of RhB monomer's LUMO splitting upon dimer formation. Based on the adsorption isotherms, obtained through the free dye molecules extraction into chloroform, and in accordance with Langmuir model, we established the effective free Gibbs energies $\triangle G_L$ which include the contribution of electrostatic interaction of dye with POM surface and weak interaction for that and between dye molecules inside the monolayer. So, they are -41.8±1.4 and -45.5±1.8 kJ/mol for ***(1)*** and ***(2)***, respectively. In order to separately distinguish the contribution of RhB-POM interactions, we carried out the fluorescence quenching titration of RhB solution by POM (to 1:1 molar ratio), and, using Stern-Volmer equation, we determined the $\triangle G_{SV}$ for such binding process: -37.4 and -39.6 kJ/mol for ***(1)*** and ***(2)***, respectively. The differences $\triangle G_L - \triangle G_{SV}$ gives the energy of intermolecular interaction for RhB forming H- and J-aggregates on POM surface. The related values are -4.4 kJ/mol (for ***(1)***) and -5.9 kJ/mol (for ***(2)***) that is much lower than $\triangle G$ of H-aggregates formation in pure RhB aqueous solution (-18.6 kJ/mol). Thus, the dimers formation inside adsorbed RhB monolayer on the POM surface is less favourable than in solution that conditions an adsorption mechanism of this dye where the H-dimers sorption is a major process as compared to monomers. The angle between transition dipole moments in J-aggregates at the final stage of supramolecular dye assembles evolution was ~ 75°. The obtained results allow us to fine tune of such hybrid structures for photovoltaic and bioinspired application where POM could be the drug carrier and RhB is release indicator.

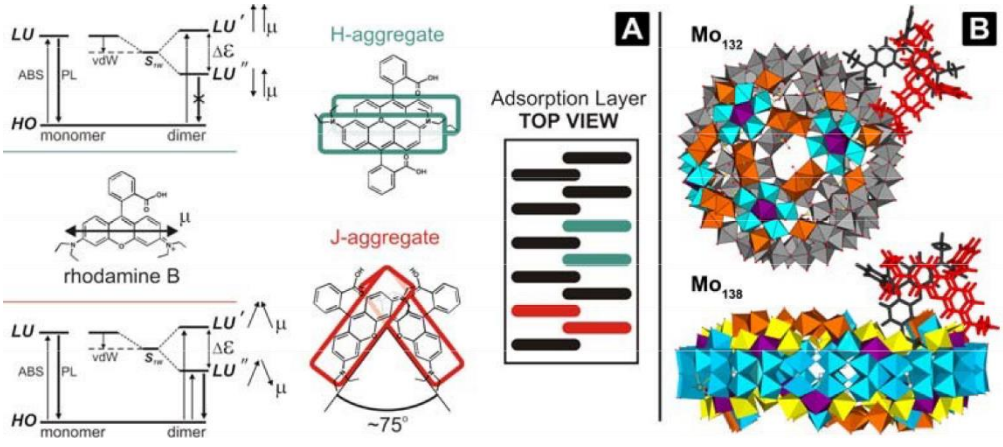

Figure 1. The model of H/J-aggregates evolution and coexistence on the POM surface.

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